

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 407 946 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90113104.5

(51) Int. Cl.⁵: C04B 35/58

(22) Date of filing: 09.07.90

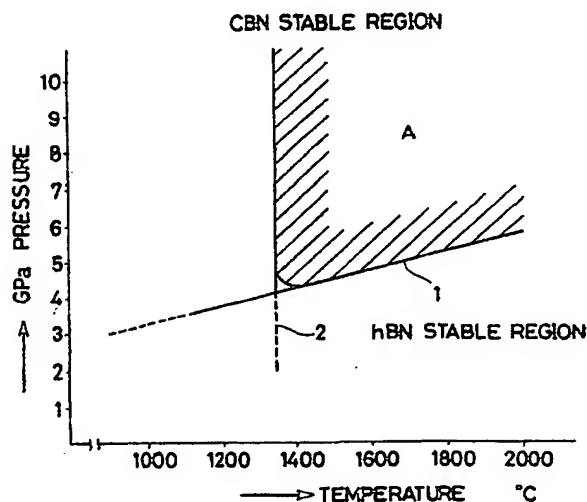
(30) Priority: 11.07.89 JP 179728/89

(43) Date of publication of application:
16.01.91 Bulletin 91/03(84) Designated Contracting States:
DE FR GB NL(71) Applicant: SUMITOMO ELECTRIC INDUSTRIES,
LIMITED
5-33, Kitahama 4-chome Chuo-ku
Osaka(JP)(72) Inventor: Sumiya, Hitoshi
c/o Itami Works of Sumitomo, Electric Ind.
Ltd.
1-1, Koyakita 1-chome, Itami-shi, Hyogo(JP)(74) Representative: Kirschner, Klaus Dieter
Patentanwälte Hermann-Trentepohl
Kirschner Grosse Bockhorni Forstenrieder
Allee 59
D-8000 München 71(DE)

(54) Cubic boron nitride sintered compact and method of preparing the same.

(57) Disclosed herein is a method of preparing a cubic boron nitride sintered compact by adding a cubic boron nitride synthetic catalyst to atmospheric pressure type boron nitride. Simultaneously with such addition of the cubic boron nitride synthetic catalyst to the atmospheric pressure type boron nitride, 0.01 to 5.0 percent by weight of a hydroxide of an alkaline earth metal is added to the atmospheric pressure type boron nitride. Then, with action of the cubic boron nitride synthetic catalyst, high temperature/high pressure treatment is performed on the atmospheric pressure type boron nitride under a thermodynamically stable pressure condition for cubic boron nitride, thereby converting the atmospheric pressure type boron nitride to cubic boron nitride. The cubic boron nitride sintered compact thus obtained contains 0.01 to 5.0 percent by weight of an oxide of the alkaline earth metal only in triple points of cubic boron nitride grains. The cubic boron nitride grains are densely bonded with each other.

FIG.1



EP 0 407 946 A1

CUBIC BORON NITRIDE SINTERED COMPACT AND METHOD OF PREPARING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a cubic boron nitride sintered compact which is applied to a cutting tool, or a heat sink material for a semiconductor laser or an LSI, for example, and a method of preparing the same.

Description of the Background Art

Cubic boron nitride (hereinafter referred to as cBN) is generally employed as a material for a cutting tool, since the same is the hardest material next to diamond and has extremely stable thermal and chemical properties. Further, cBN is excellent in thermal conductivity after diamond, and expected is application of cBN to a heat sink (radiation substrate) for a semiconductor laser or the like. However, it is extremely difficult to prepare a large-sized single crystal of cBN, and hence a sintered compact formed of cBN grains of several micrometers is watched as a practicable material.

Since it is extremely difficult to directly sinter cBN grains (powder) independently, a metal such as Al or Co, a carbide such as TiC, or a nitride such as TiN is generally employed as a binder for sintering the cBN grains. In a cBN sintered compact containing the aforementioned binder, however, the binder defines a continuous phase among the cBN grains, and hence hardness and thermal conductivity of the sintered compact are so significantly reduced that it is difficult to sufficiently effectuate excellent properties originally provided in cBN.

Japanese Patent Laying-Open No. 54-33510 or Material Research Bulletin, Vol. 7 (1972), pp. 999 to 1004 discloses a known method of preparing a cBN sintered compact containing no binder with a starting material of atmospheric pressure type BN (hexagonal boron nitride: hereinafter referred to as hBN) by directly converting hBN to cBN under superhigh pressure/temperature conditions of 6.5 GPa and at least 1800°C and simultaneously sintering the same. However, such a method of preparing a cBN sintered compact by direct conversion requires extremely high pressure/high temperature conditions while the same is insufficient in reproducibility, to cause problems in industrial production.

On the other hand, each of Japanese Patent Laying-Open Nos. 58-176179 and 59-57967

(Japanese Patent Publication Nos. 59-5547 and 60-28782) discloses a method which can prepare a cBN sintered compact under relatively mild pressure/temperature conditions as compared with the aforementioned direct conversion method with excellent reproducibility. According to this method, a small quantity of alkaline earth metal boron nitride is added to or diffused/contained in hBN powder or a sintered compact thereof, which in turn is treated under a thermodynamically stable pressure condition for hBN at a temperature exceeding 1350°C. This method is adapted to convert hBN to cBN with a catalyst of the alkaline earth metal boron nitride while bonding the cBN grains with each other simultaneously with such conversion. It is said that, according to this method, the material can be treated at a temperature exceeding 1350°C, which is the eutectic temperature of the alkaline earth metal boron nitride and hBN, to obtain a strong sintered compact which is formed of only cBN grains of 3 to 10 μm in unit grain diameter containing substantially no impurity.

U. S. Patent No. 4,772,575 also discloses a method of preparing a cBN sintered compact using alkaline earth metal boron nitride as a catalyst. In the method disclosed in U. S. Patent No. 4,772,575, a sintered compact of cubic boron nitride is made by adsorbing and/or diffusing 0.005 to 1.000 percent by weight of water into a boron nitride compact containing alkaline earth metal boron nitride as a catalyst.

The inventor has experimentally prepared a cBN sintered compact by the aforementioned method using the alkaline earth metal boron nitride, to make a cutting test with the as-formed sintered compact. As the result, it has been recognized that the cBN sintered compact was so extremely worn by falling of cBN grains and transgranular rupture that no expected performance was attained. The maximum thermal conductivity of this cBN sintered compact was 6 w/cm·°C, which was twice or three times excellent as compared with BeO (beryllium oxide) or AlN (aluminum nitride) generally employed for a heat sink material. However, it has also been recognized that this cBN sintered compact was rather largely dispersed in thermal conductivity, which is the most important basic property of a heat sink material.

In order to solve this problem, the inventor has made deep study on the cBN sintered compact obtained by the aforementioned method, to recognize that unit grains forming the cBN sintered compact were irregular and this disadvantage was promoted as abnormal grain growth was increased. Such irregularity of the grains easily leads to falling

of the grains and transgranular rupture (cleavage), to reduce wear resistance and strength (toughness) of the sintered compact. Further, denseness of the sintered compact is deteriorated to increase phonon scattering at grain boundaries, whereby thermal conductivity is reduced.

The aforementioned conventional method uses the alkaline earth metal boron nitride as a catalyst for converting hBN to cBN in a eutectic state with BN, and hence states of generation of cBN cores and following growth of cBN crystal grains are significantly varied with the dispersed state of the catalyst, the treatment temperature and fine pressure variation. According to this method, therefore, partial abnormal grain growth of cBN grains easily takes place and hence it is extremely difficult to control configurations and sizes of the grains.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a cBN sintered compact having a dense and homogeneous structure, which is suitable for a material for a cutting tool or a heat sink, by controlling the sizes and configurations of cBN grains.

The inventive method of preparing a cBN sintered compact comprises the steps of:

- (1) adding a cBN synthetic catalyst to atmospheric pressure type boron nitride (normal hBN) and further adding 0.01 to 5.0 percent by weight of a hydroxide of an alkaline earth metal to the raw material of the atmospheric pressure type boron nitride; and
- (2) performing high temperature/high pressure treatment on the raw material under a thermodynamically stable pressure condition for cBN at a temperature exceeding a level capable of converting the atmospheric pressure type boron nitride to cBN with action of the cBN synthetic catalyst.

The as-formed cBN sintered compact contains 0.01 to 5.0 percent by weight of an oxide of the alkaline earth metal, and cBN grains are densely bonded with each other. The inventive cBN sintered compact is particularly characterized in that the oxide of the alkaline earth metal is interspersed among triple points of the cBN grains.

The atmospheric pressure type boron nitride, serving as a raw material, is generally prepared from hBN, while rhombohedral boron nitride (rBN), amorphous boron nitride (aBN) or pyrolytic boron nitride (pBN) is also employable. Purity of such a raw material must be as high as possible, while the content of B_2O_3 , in particular, is preferably not more than 0.3 percent by weight, so that the same will not prevent conversion of hBN to cBN.

The cBN synthetic catalyst may be prepared

from a well-known material, preferably from an alkaline metal boron nitride or an alkaline earth metal boron nitride or an alkaline earth metal. The content of the catalyst is within a range of 0.01 to 5.0 mole percent with respect to the raw material of atmospheric pressure type boron nitride. If the content of the catalyst is not more than 0.01 mole percent, conversion of hBN to cBN is not sufficiently promoted. If the content exceeds 5.0 mole percent, on the other hand, a large quantity of the catalyst is left in the cBN sintered body to extremely reduce mechanical properties and thermal conductivity of the cBN sintered compact.

A hydroxide ($Me(OH)_2$) of an alkaline earth metal such as $Mg(OH)_2$ or $Ca(OH)_2$, for example, is added in order to suppress abnormal grain growth of cBN. The content of such an admixture is within a range of 0.01 to 5.0 percent by weight with respect to the raw material of atmospheric pressure type boron nitride. A sufficient effect cannot be attained if the content of the admixture is not more than 0.01 percent by weight, while a large quantity of oxide of the alkaline earth metal such as MgO or CaO , for example, is left in the cBN sintered compact if the content exceeds 5.0 percent by weight, to reduce mechanical performance and thermal conductivity of the cBN sintered body.

The aforementioned atmospheric pressure type boron nitride mixed with the cBN synthetic catalyst and the hydroxide of the alkaline earth metal is treated with a high temperature/high pressure generator under a thermodynamically stable pressure condition for cBN at a temperature exceeding a level capable of converting the atmospheric pressure type boron nitride to cBN with action of the cBN synthetic catalyst, such as a temperature exceeding $1350^\circ C$ if the cBN synthetic catalyst is prepared from magnesium boron nitride, for example. Fig. 1 is a graph showing an hBN-cBN thermal equilibrium curve. Referring to Fig. 1, a cBN stable region appears above a line 1 and an hBN stable region appears under the line 1, while numeral 2 denotes a eutectic line of the magnesium boron nitride and boron nitride (BN). In this case, therefore, treatment is performed in a region A shown in Fig. 1 at a temperature exceeding $1350^\circ C$.

Upon the aforementioned treatment, the atmospheric pressure type boron nitride is converted to cubic boron nitride (cBN) simultaneously with sintering of cBN grains. At this time, the alkaline earth metal hydroxide ($Me(OH)_2$, Me: alkaline earth metals) added to the raw material is decomposed into an oxide (MeO) of the alkaline earth metal. The generated MeO blocks floating of eutectic materials to suppress abnormal grain growth of cBN. Further, the generated MeO is not left in boundaries between cBN grains but interspersed among triple points. In the as-formed cBN sintered compact,

therefore, all cBN grains are continuously bonded with each other so that characteristics such as hardness and thermal conductivity are not influenced by the residual MeO. Further, the cBN sintered compact is dense with uniform grain diameters.

As hereinabove described in detail, the present invention is adapted to obtain a cBN sintered compact by adding a cBN synthetic catalyst and a hydroxide of an alkaline earth metal to atmospheric pressure type boron nitride and treating the same under high pressure/high temperature conditions. According to the present invention, it is possible to obtain a cBN sintered compact which has a dense and homogeneous structure with strongly bonded cBN grains by simply adding the hydroxide of the alkaline earth metal to the raw material, dissimilarly to the conventional methods. The as-formed cBN sintered compact, which has mechanical properties superior to those of conventional ones, can be applied to a cutting tool and the like. Further, the cBN sintered compact has such high thermal conductivity that the same is optimum as a heat sink material. Thus, the present invention has great effects as a cBN sintered compact and a method of preparing the same.

These and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing temperature-pressure equilibrium in the case of employing magnesium boronitride as a cBN synthetic catalyst, for illustrating a region capable of preparing a cBN sintered compact according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Powder of hBN containing 0.2 percent by weight of B_2O_3 , powder of magnesium boron nitride (Mg_3BN_3) and magnesium hydroxide ($Mg(OH)_2$) were sufficiently mixed in nitrogen gas in the ratios 95.5:4:0.5 in weight percentage. In this case, the content of magnesium boron nitride with respect to hBN was about 1 mole percent.

This mixture was embossed, subjected to high pressure/high temperature treatment with a girdle type high temperature/high pressure generator un-

der pressure and temperature conditions of 5.5 GPa and $1500^\circ C$, and then quenched to take out the product.

The as-formed sample was a strong gray sintered compact. It was proved by X-ray diffraction that this sample was a cBN sintered compact, while a small quantity of MgO and an extremely trace quantity of Mg_3BN_3 high-pressure phase were detected. The surface of this cBN sintered compact was observed with a scanner type electron microscope (SEM), to recognize that cBN grains having relatively uniform grain diameters of 5 to 8 μm were continuously bonded in a dense structure. The compact was further observed with a transmission type electron microscope (TEM), to recognize that MgO was interspersed among only triple points of the cBN grains.

Thermal conductivity and Vickers hardness of the aforementioned sintered compact were measured at the room temperature, to recognize high values of $6.5 \text{ w/cm}^\circ C$ and 6000 to 6500 kg/mm^2 respectively.

For the purpose of comparison, 1 mole percent of Mg_3BN_3 powder was added to hBN powder, and the mixture was subjected to high temperature/high pressure treatment under the same conditions as above with no addition of $Mg(OH)_2$, to prepare a cBN sintered compact. The structure of this cBN sintered compact was observed with a scanner type electron microscope (SEM), to recognize that the cBN grains had rather irregular grain diameters of 3 to 10 μm although the grains were bonded with each other, while coarse grains having diameters of 20 to 30 μm were partially observed. Thermal conductivity and Vickers hardness of this sample were $5.3 \text{ w/cm}^\circ C$ and 5000 to 6500 kg/mm^2 respectively. These values were dispersed low as compared with the inventive sample.

Example 2

Similarly to Example 1, 1 mole percent of Mg_3BN_3 and 1.2 percent by weight of $Mg(OH)_2$ were added to hBN powder, and this mixture was subjected to high pressure/high temperature treatment for 30 minutes under pressure and temperature conditions of 5.0 GPa and $1400^\circ C$, to obtain a sintered compact.

This sintered compact had an extremely dense and homogeneous structure, which was formed of fine cBN grains of about 1 μm in diameter. Although this sintered compact exhibited rather low thermal conductivity of $4.5 \text{ w/cm}^\circ C$, its Vickers hardness was at a high value of 6500 kg/mm^2 . This sintered compact was cut with a laser, to produce a cutting tool.

For the purpose of comparison, a cutting tool

of the same configuration was produced by a commercially available cBN sintered compact (bonded member) which was prepared by bonding cBN grains of 3 μm in mean grain size with a binder mainly formed of TiN. This cBN sintered compact contained about 30 percent by volume of the binder.

The aforementioned cutting tools were subjected to a cutting test of cutting members of gray cast iron (F25) under conditions of a cutting speed of 500 m/min., depth of cut of 0.2 mm, and a feed rate of 0.1 mm/rev.

The former cutting tool produced by the inventive sintered compact was capable of performing cutting for 40 minutes before a wear width at its tip flank reached 0.1 mm. In the latter cutting tool produced by the commercially available sintered compact, on the other hand, the flank wear width reached 0.1 mm upon cutting for about 15 minutes.

Example 3

Similarly to Example 1, 1.2 mole percent of calcium boron nitride and 1.0 percent by weight of $\text{Ca}(\text{OH})_2$ were added to hBN powder, and the mixture was subjected to high pressure/high temperature treatment for 30 minutes under pressure and temperature conditions of 5.5 GPa and 1450 °C.

The as-formed cBN sintered compact exhibited regular unit grain diameters of 5 to 8 μm , and the cBN grains were strongly bonded with each other. Further, CaO was homogeneously interspersed among triple points of the cBN grains. This sintered compact had high thermal conductivity and Vickers hardness of 6.0 $\text{w/cm}^2 \cdot ^\circ\text{C}$ and 5000 to 6500 kg/mm^2 respectively.

For the purpose of comparison, a cBN sintered compact was prepared under the same conditions as above with no addition of $\text{Ca}(\text{OH})_2$. This cBN sintered compact exhibited irregular grain diameters of 5 to 30 μm and fine cracks were partially observed in the sintered compact, while thermal conductivity and hardness were so inferior that the same were not worth measuring.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. A cubic boron nitride sintered compact obtained by adding a synthetic catalyst of cubic boron

nitride to atmospheric pressure type boron nitride and performing high temperature/high pressure treatment on the mixture, said cubic boron nitride sintered compact containing 0.01 to 5.0 percent by weight of an oxide of an alkaline earth metal and being formed of cubic boron nitride grains densely bonded with each other.

2. A cubic boron nitride sintered compact in accordance with claim 1, wherein

said oxide of said alkaline earth metal is discontinuously interspersed within a matrix of said cubic boron nitride grains in said cubic boron nitride sintered compact.

3. A cubic boron nitride sintered compact in accordance with claim 1, wherein

said oxide of said alkaline earth metal is present only in triple points of said cubic boron nitride grains.

4. A cubic boron nitride sintered compact in accordance with claim 1, wherein

said atmospheric pressure type boron nitride is hexagonal cubic boron nitride containing not more than 0.3 percent by weight of B_2O_3 ,

said cubic boron nitride synthetic catalyst is an alkaline metal boron nitride or an alkaline earth metal boron nitride, and

the quantity of said cubic boron nitride synthetic catalyst with respect to said atmospheric pressure type boron nitride is within a range of 0.01 to 5.0 mole percent.

5. A cubic boron nitride sintered compact in accordance with claim 1, wherein

grain diameters of said cubic boron nitride grains are not more than 8 μm and difference between the maximum and minimum grain diameters is not more than 3 μm ,

thermal conductivity of said cubic boron nitride sintered compact is within a range of 4.5 to 6.5 $\text{w/cm}^2 \cdot ^\circ\text{C}$, and

Vickers hardness of said cubic boron nitride sintered compact is within a range of 5000 to 6500 kg/mm^2 .

6. A cubic boron nitride sintered compact obtained by adding a cubic boron nitride synthetic catalyst to atmospheric pressure type boron nitride and performing high temperature/high pressure treatment on the mixture,

said cubic boron nitride sintered compact containing 0.01 to 5.0 percent by weight of an alkaline earth metal in only triple points of cubic boron nitride grains,

grain diameters of said cubic boron nitride grains being not more than 8 μm , with difference between maximum and minimum grain diameters being not more than 3 μm .

7. A method of preparing a cubic boron nitride sintered compact by adding a cubic boron nitride synthetic catalyst to atmospheric pressure type bo-

ron nitride, said method comprising the steps of:
adding said cubic boron nitride synthetic catalyst
and 0.01 to 5.0 percent by weight of a hydroxide of
an alkaline earth metal to said atmospheric pres-
sure type boron nitride; and

5

performing high pressure/high temperature treat-
ment on the mixture under a thermodynamically
stable pressure condition for cubic boron nitride at
a temperature exceeding a level capable of con-
verting said atmospheric pressure type boron
nitride to cubic boron nitride with action of said
cubic boron nitride synthetic catalyst.

10

8. A method of preparing a cubic boron nitride
sintered compact in accordance with claim 7,
wherein

15

said synthetic catalyst is prepared from an alkaline
metal boron nitride or an alkaline earth metal boron
nitride and added to said atmospheric pressure
type boron nitride in a quantity within a range of
0.01 to 5.0 mole percent.

20

9. A method of preparing a cubic boron nitride
sintered compact in accordance with claim 7,
wherein a magnesium boron nitride or a calcium
boron nitride is employed as said synthetic catalyst
and $Mg(OH)_2$ or $Ca(OH)_2$ is employed as said
hydroxide of said alkaline earth metal.

25

10. A method of preparing a cubic boron nitride
sintered body, comprising the steps of:

adding an alkaline metal boron nitride or an alkaline
earth metal boron nitride to atmospheric pressure
type boron nitride containing not more than 0.3
percent by weight of B_2O_3 in a quantity within a
range of 0.01 to 5.0 mole percent with respect to
said atmospheric pressure type boron nitride;

30

adding a hydroxide of an alkaline earth metal to
said atmospheric pressure type boron nitride in a
quantity within a range of 0.01 to 5.0 percent by
weight with respect to said atmospheric pressure
type boron nitride; and

35

performing high temperature/high pressure treat-
ment on said atmospheric pressure type boron
nitride with catalytic action of said alkaline metal
boron nitride or said alkaline earth metal boron
nitride under a thermodynamically stable pressure
condition for cubic boron nitride, thereby convert-
ing said atmospheric pressure type boron nitride to
cubic boron nitride.

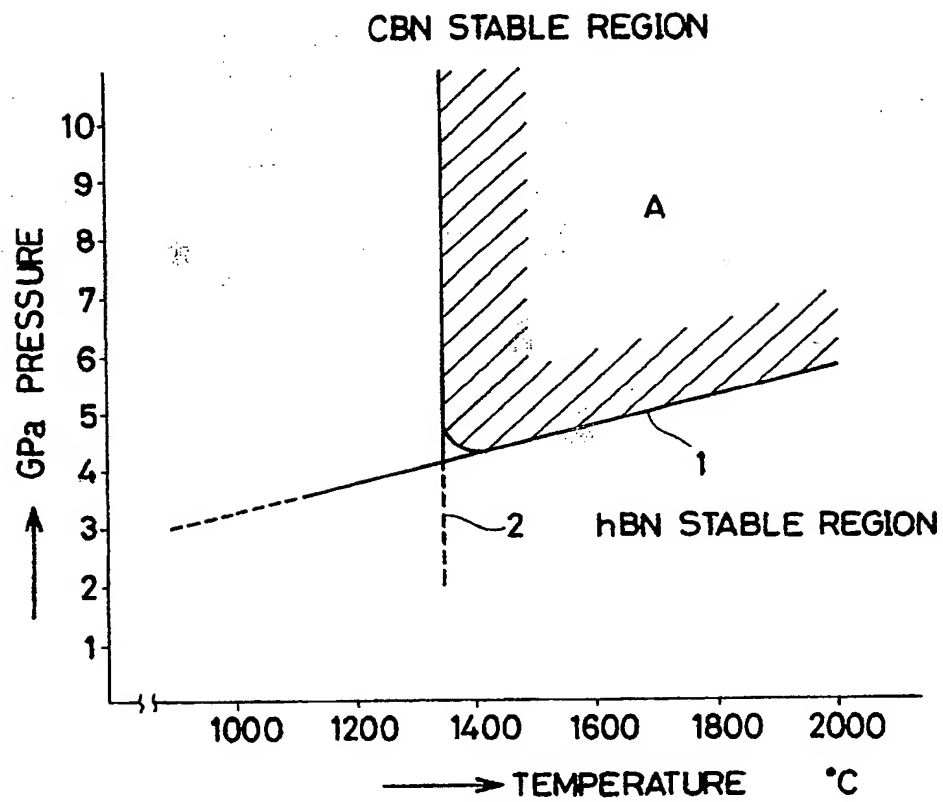
40

45

50

55

FIG.1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 3104

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-3 030 362 (INSTITUT SVERCHTVERDYCH MATERIALOV AKADEMII NAUK UKRAINSKOJ SSR) * Claims 1,3,6; page 3, paragraph 2; page 8, paragraph 2 *	1,7-10	C 04 B 35/58
X	DE-A-2 500 515 (HITACHI, LTD) * Claims 1,5; page 6, paragraph 3 - page 7, paragraph 2 *	1,5	
A,D	EP-A-0 240 913 (SUMITOMO ELECTRIC INDUSTRIES LTD) * Claims 1-5; page 5, paragraph 4; table 1 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 04 B 35/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-08-1990	Examiner HAUCK, H.N.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	